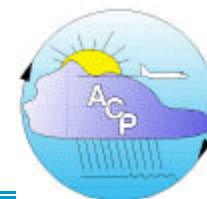# Nighttime Chemistry: Possible Evidence of Heterogeneous Loss Processes?

Carl Berkowitz[1], Chet Spicer[2], Rahul Zaveri[1] Rob Disselkamp[1,] Elaine Chapman[1], Jim Cowin[1], Jeff Gaffney[3], Nels Laulainen[1], Nancy Marley[3], Bob Plastridge[2],

1) **Pacific Northwest National Laboratory**

2) **Battelle Columbus Laboratory**

3) **Argonne National Laboratory**

The Problem:
uncertainties in air quality modeling due to aerosol/oxidant interactions

- Do heterogeneous reactions of ozone and NOy species on aerosol surfaces significantly effect gas-phase concentrations?

- Is NOx regenerated from HNO3 + aerosol reactions?

- Working hypothesis: biggest effect at night (no competing photochemistry and low turbulent mixing:

- **Laboratory Studies**: to elucidate nitrogen reaction kinetics

- **Field Campaigns**: to look for evidence to support or disprove hypothesis that these processes occur.

- **Modeling Analysis**: can laboratory results explain field observations?

Objectives of the Instrument Testing Experiment (ITEX)

Moonrise over the G-1
(photo by Nancy Marley/ANL)

1) Testing and evaluation of
   – New mass spectrometer (Battelle Columbus)
   – New NO2/PAN system (Argonne National Laboratory)
   – Multi-wavelength nephelometry system (PNNL and U/Wash.)
   – Single aerosol sampling system (PNNL)

2) Feasibility of nighttime flight procedures

3) To collect ozone, aerosol and NOy data in support of testing the hypothesis: heterogeneous reactions were occurring over the sampling domain.

Logistics of Field Program

- Test sampling over Columbia Basin and Portland, Oregon, between August 25 and September 13, 1998

- G-1 based at RAF facility in Pasco, WA. 30 minute ferry to Portland

- For nighttime sampling:

  – depart from Pasco ~ 9PM; sample in Portland vicinity (~80 minute, with flight plan shown in following schematic, return to Pasco)
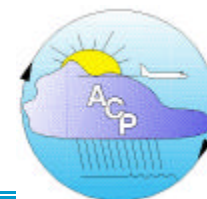
  – refuel rest-up and repeat, departing ~2AM

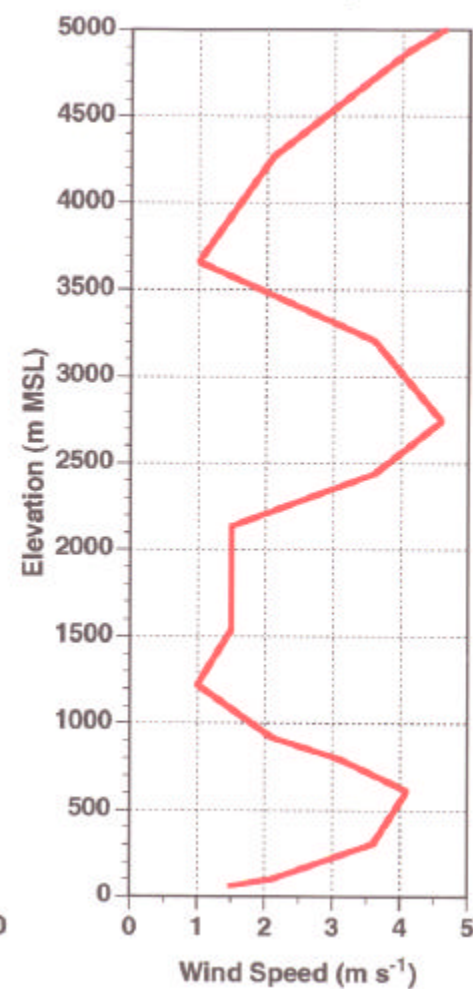# Nighttime Field Studies
Evidence that heterogeneous chemistry occurs?

Prevailing 850 mb wind

4000 ft MSL

3000 ft MSL

Nocturnal Stable Layer
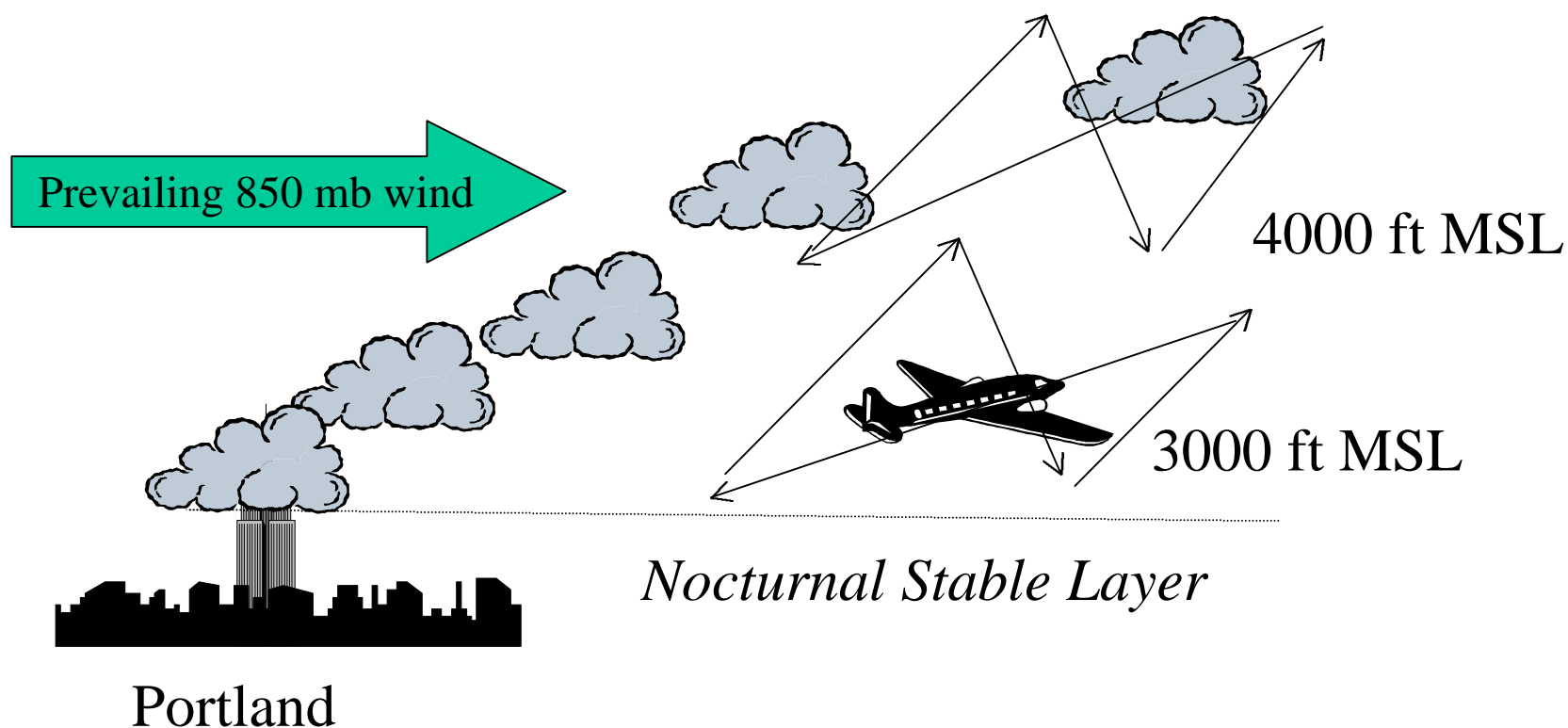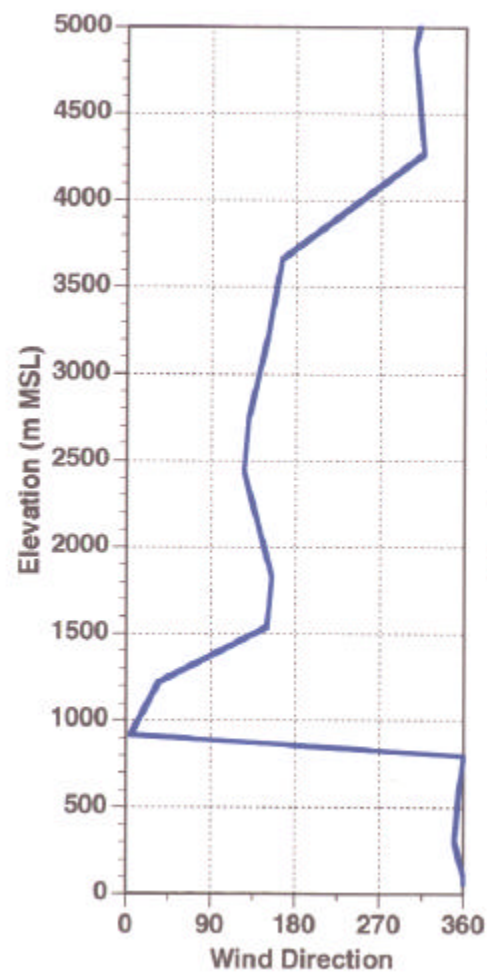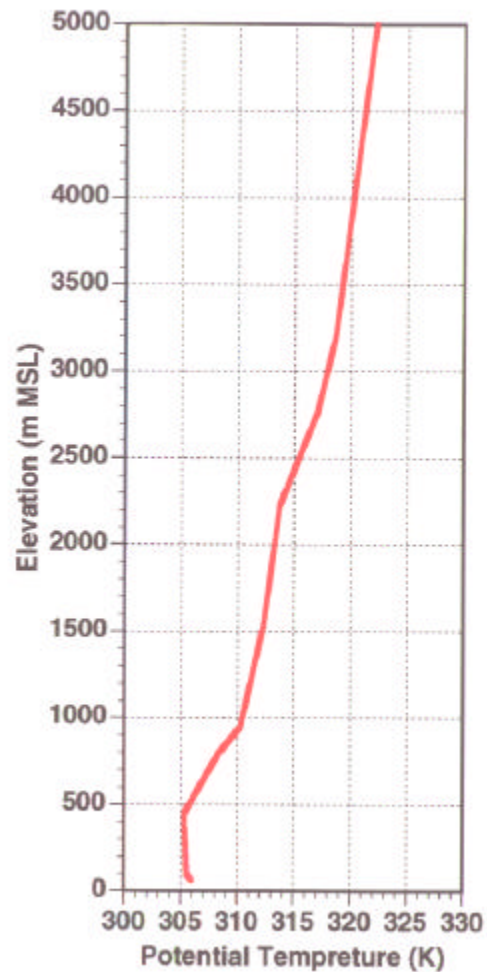
Portland

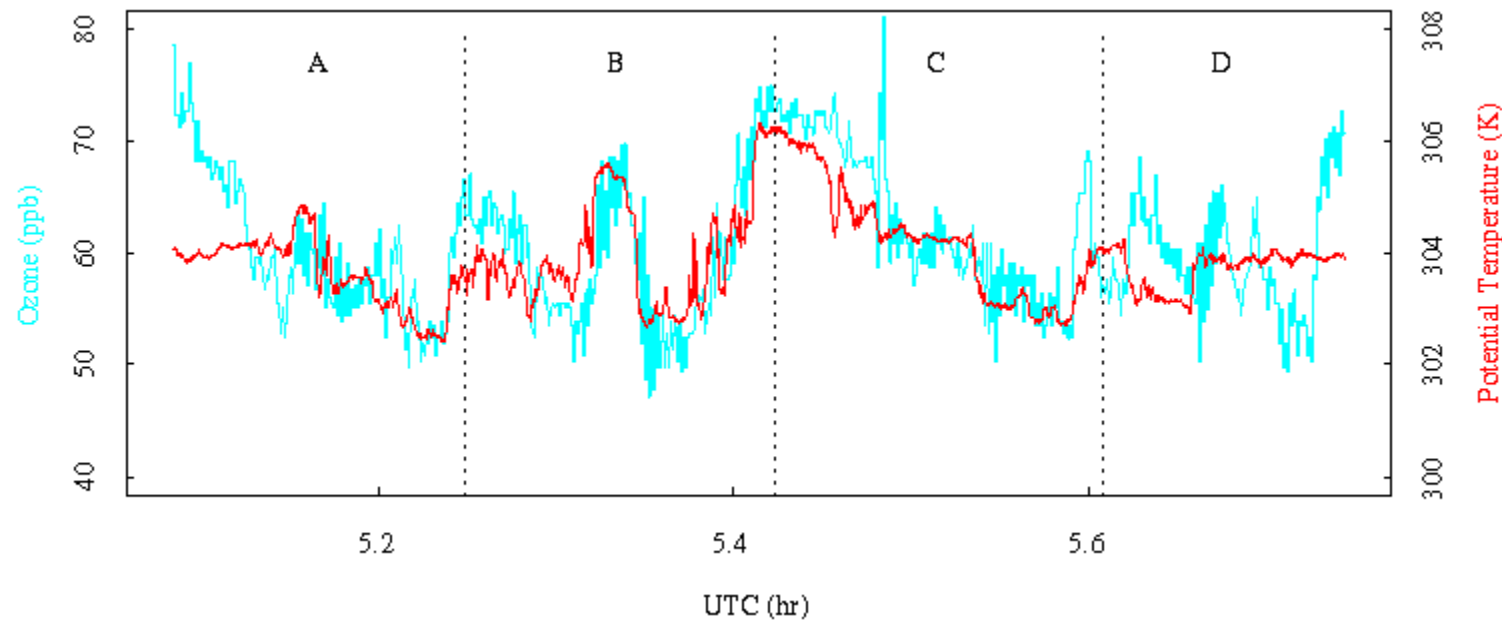Sampling was done downwind of Portland, OR, at two altitudes; once after sunset, and again several hours later.

Sep 1, 1998, Flight A, 3000 ft MSL

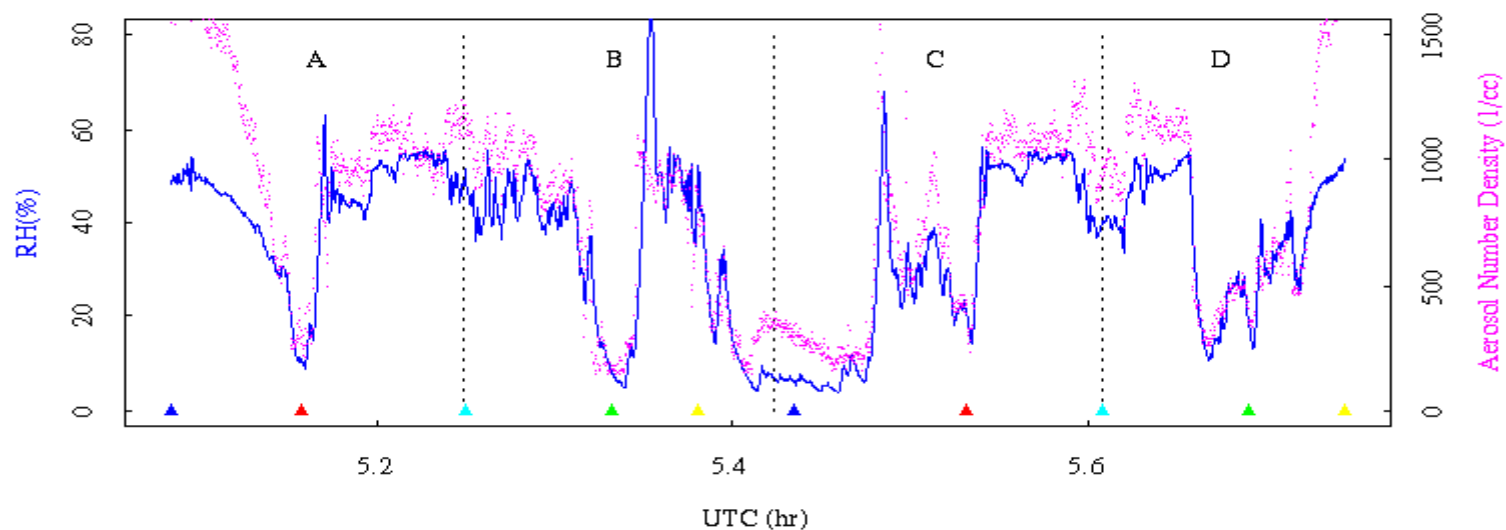Sep 1, 1998, 00 UTC, SALEM,OR (44.92N, 123.02W, 61mMSL)
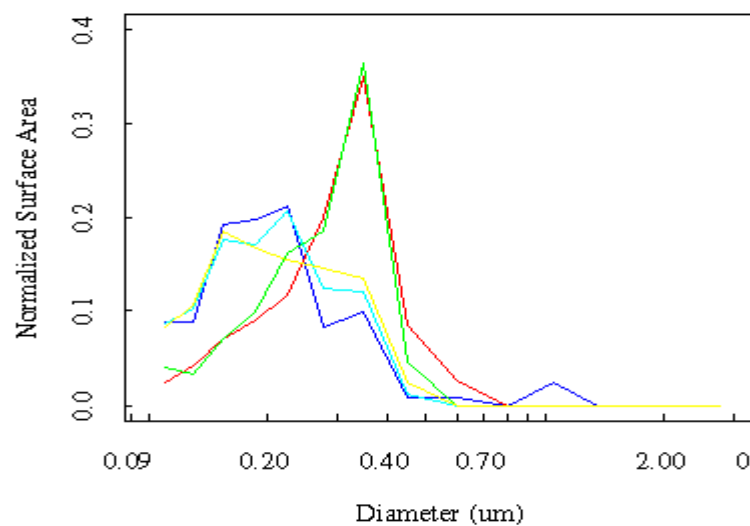
Sep 1, 1998, Flight A, 3000 ft MSL

• Ozone and potential temperature are well correlated
• RH and aerosol number density also appear to be strongly correlated
• Anti-correlation exists between ozone and aerosol number density in patches
• Samples with low ozone and low aerosol number density also display a different surface area (or number) size distribution shape, suggesting a different origin than the rest of the air mass
• Variations in ozone appears to be mostly due to meteorological factors as suggested by strong positive correlation between ozone and potential temperature.
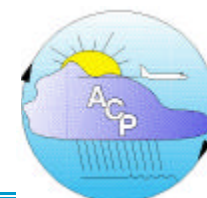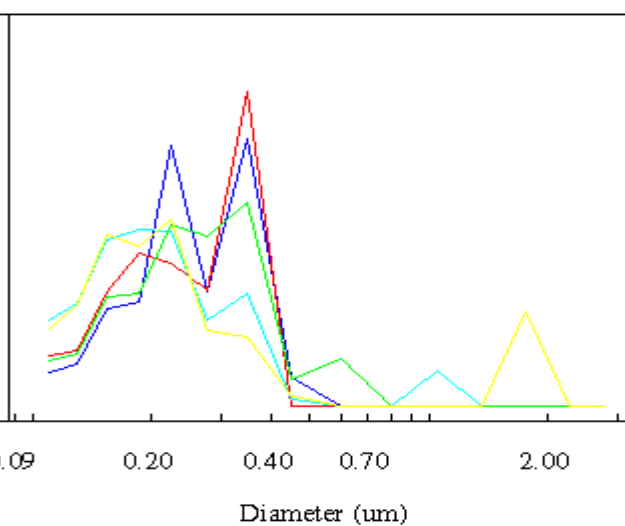
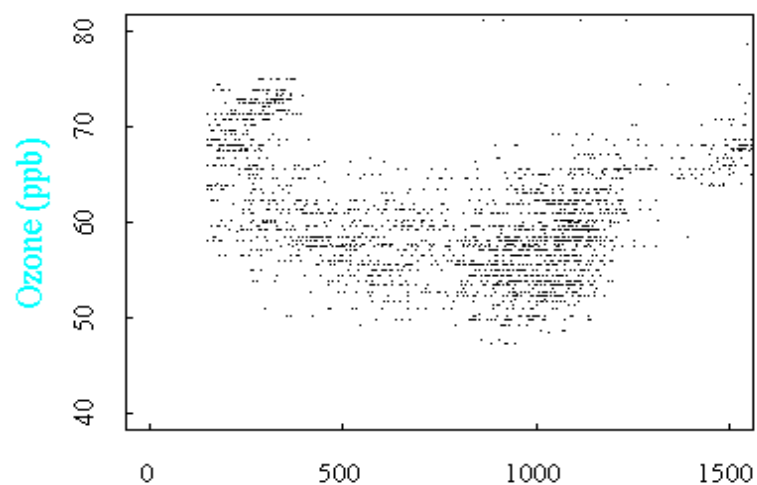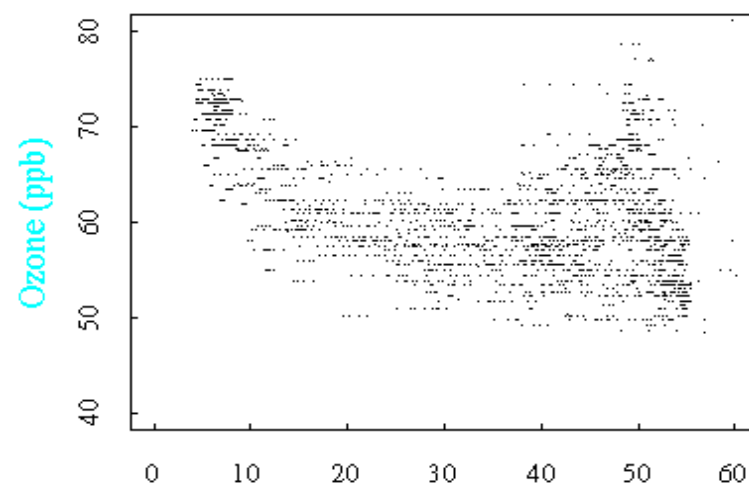Sep 1, 1998, Flight A, 3000 ft MSL

Segments A and B

Segments C and D

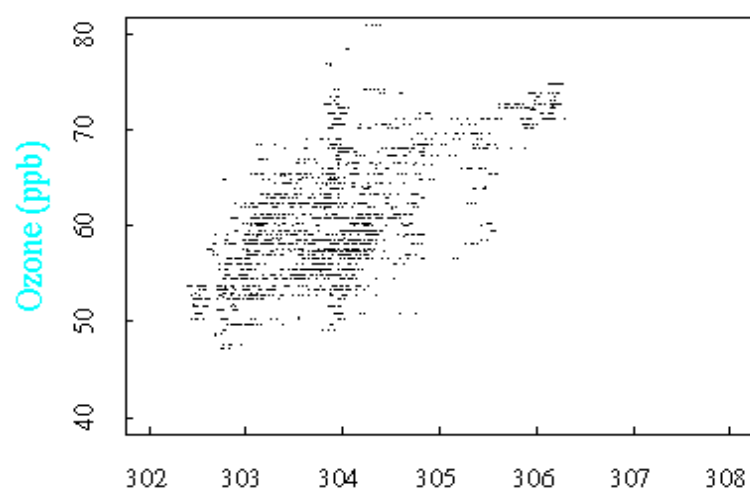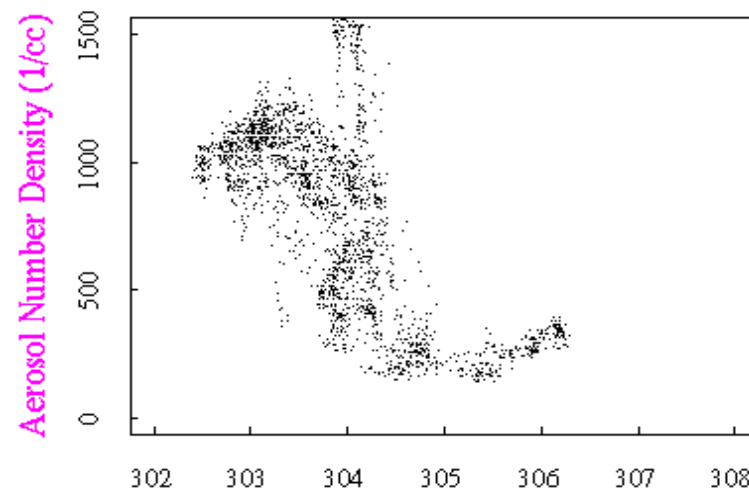Sep 1, 1998, Flight A, 3000 ft MSL

Portland

Flight Path

Salem

I5

A

B
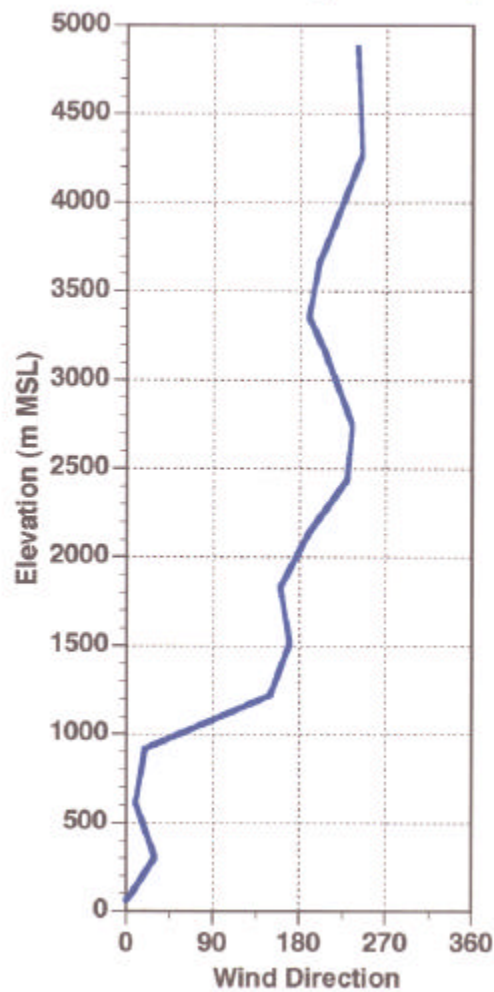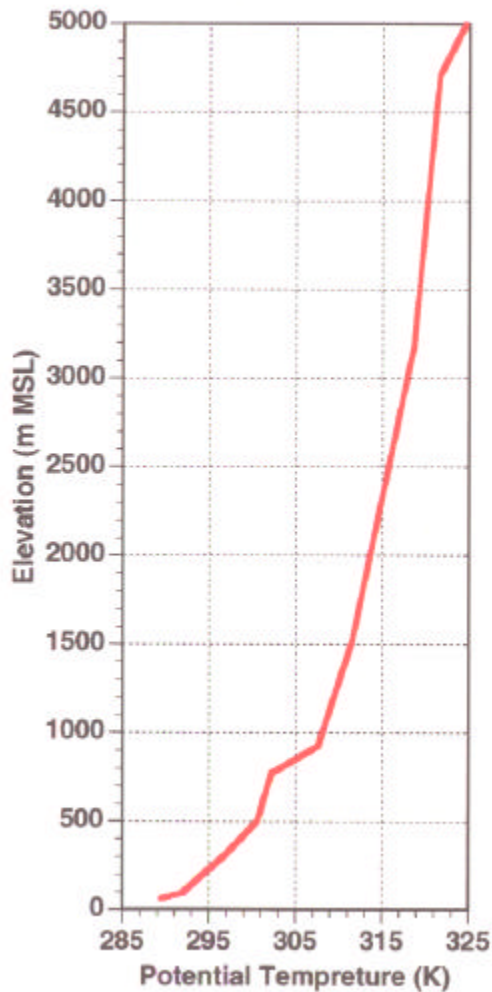
C

D
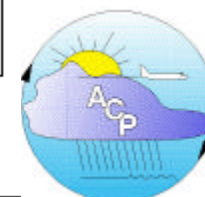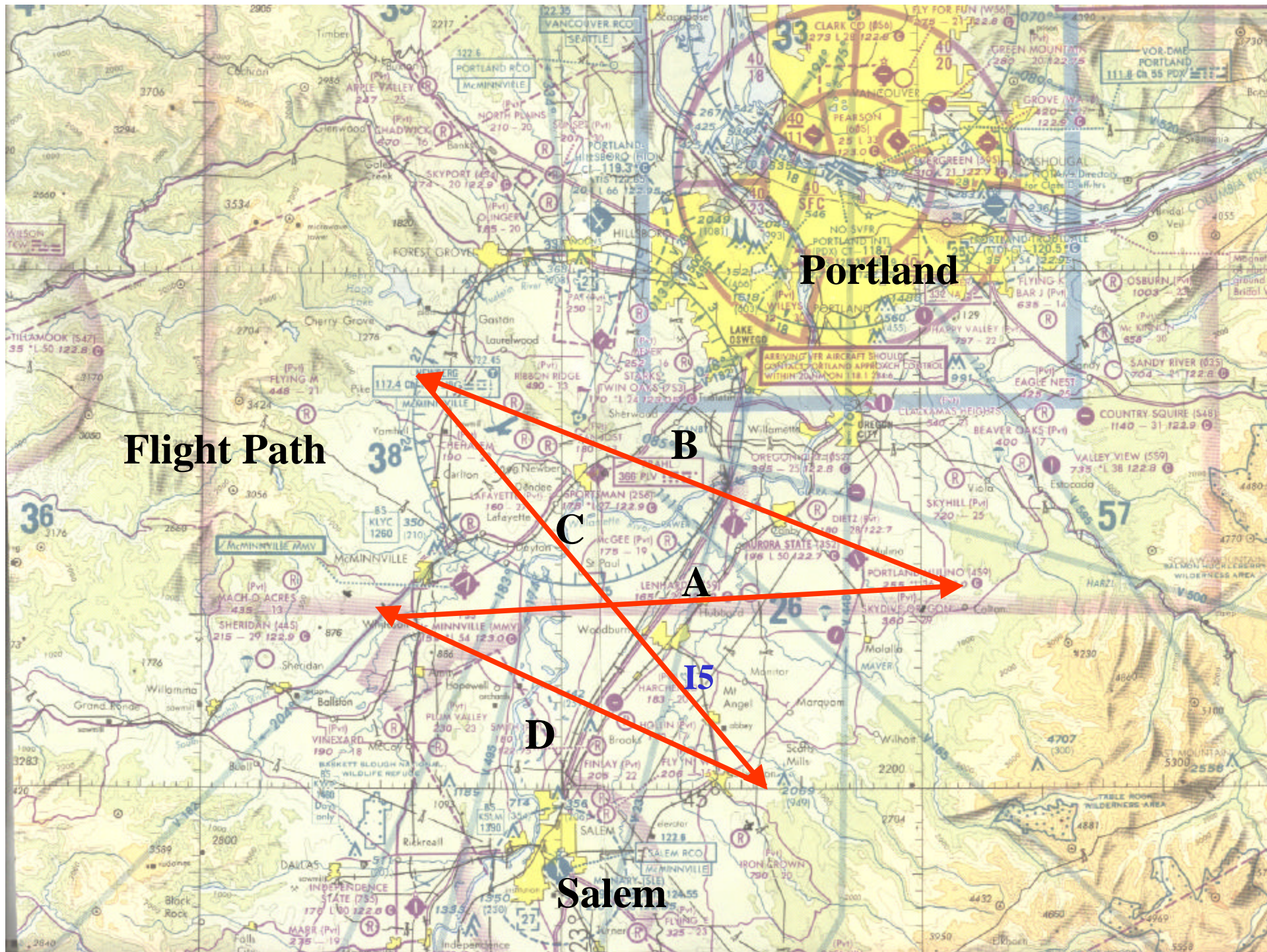
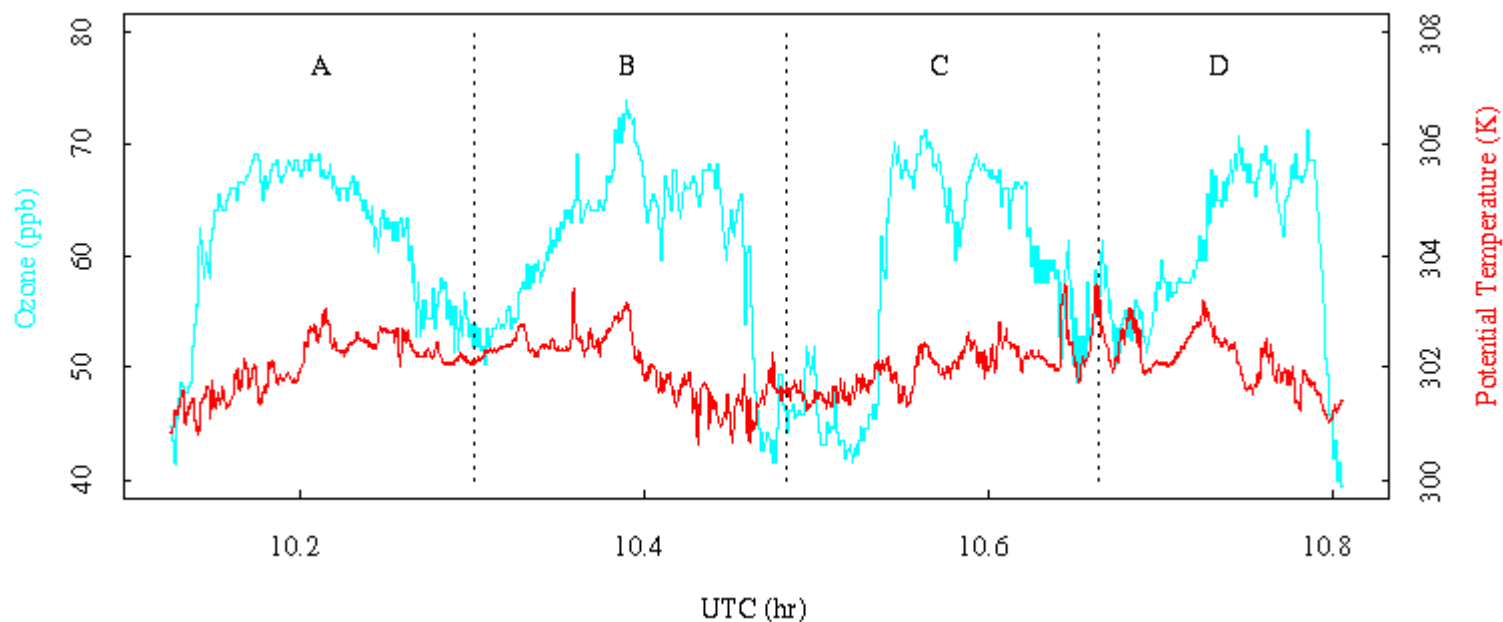# Sep 1, 1998, Flight B, 3000 ft MSL

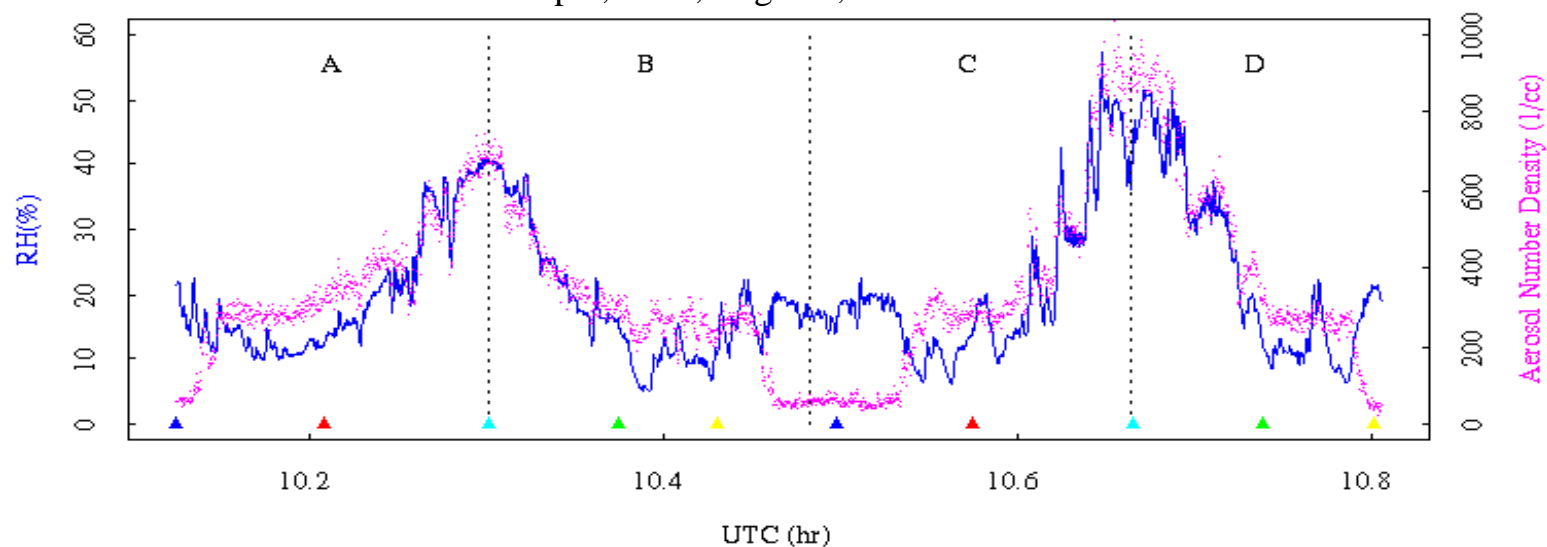Sep 1, 1998, 12 UTC, SALEM,OR (44.92N, 123.02W, 61mMSL)
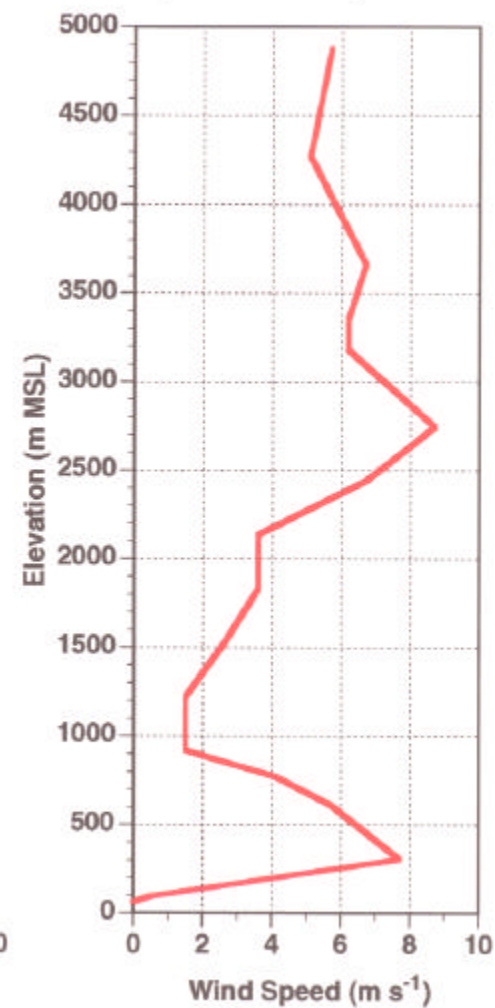
Sep 1, 1998, Flight B, 3000 ft MSL

- Ozone and potential temperature appear to be weakly anti-correlated
- Strong correlation persists between RH and aerosol number density
- Good anti-correlation is observed between ozone and aerosol number density as well as between ozone and RH
- Samples with very low ozone and low aerosol number density display different surface area size distribution shapes, suggesting different origin(s)
- Variation of ozone appears to be due to heterogeneous loss on aerosol surface because of significant anti-correlation between ozone and surface area (or number density) and also due to weak anti-correlation between ozone and potential temperature.
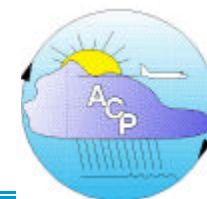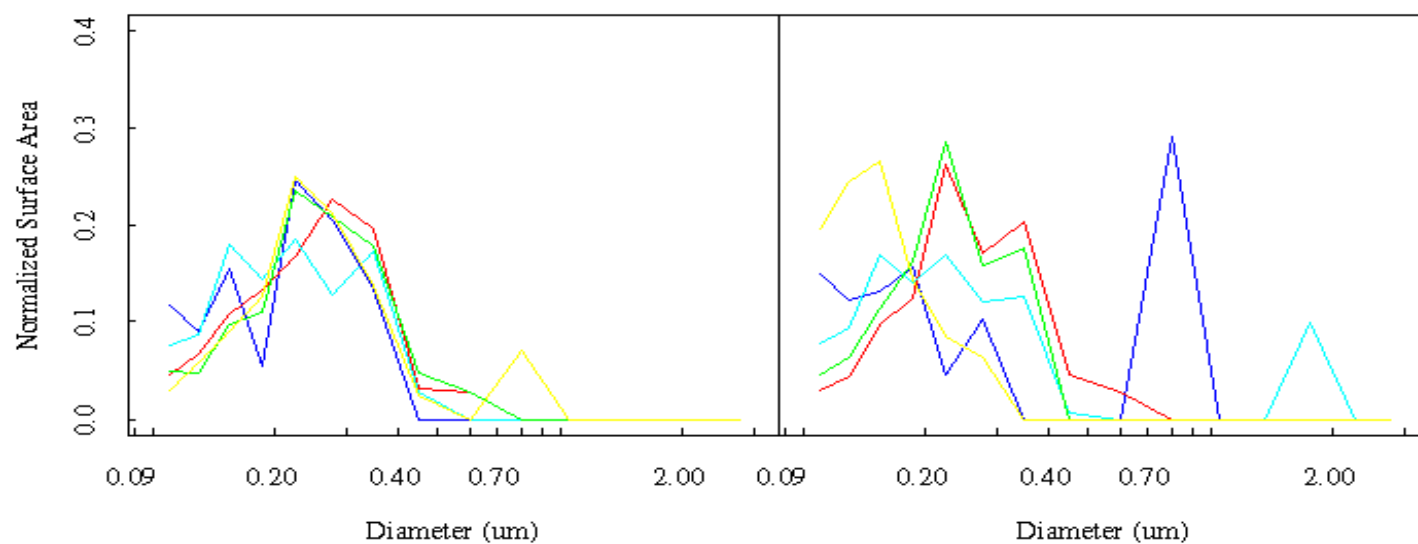
Sep 1, 1998, Flight B, 3000 ft MSL

Pacific Northwest National Laboratory

Sep 1, 1998, Flight B, 3000 ft MSL
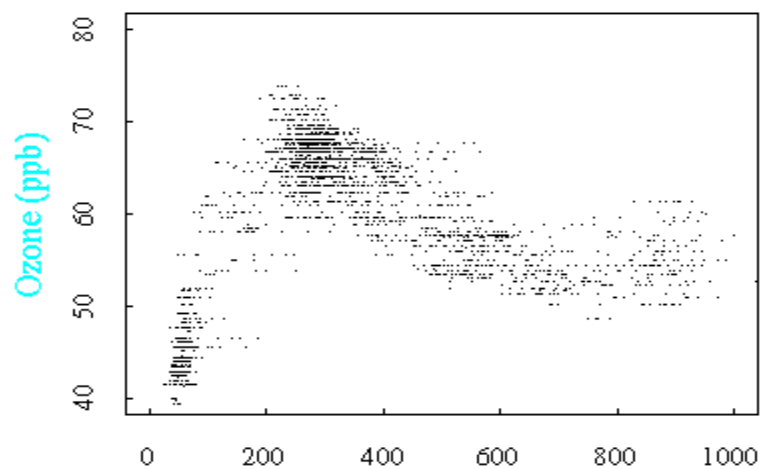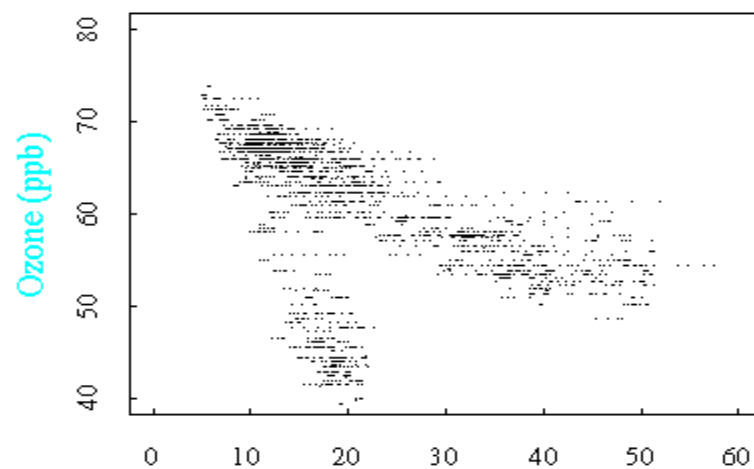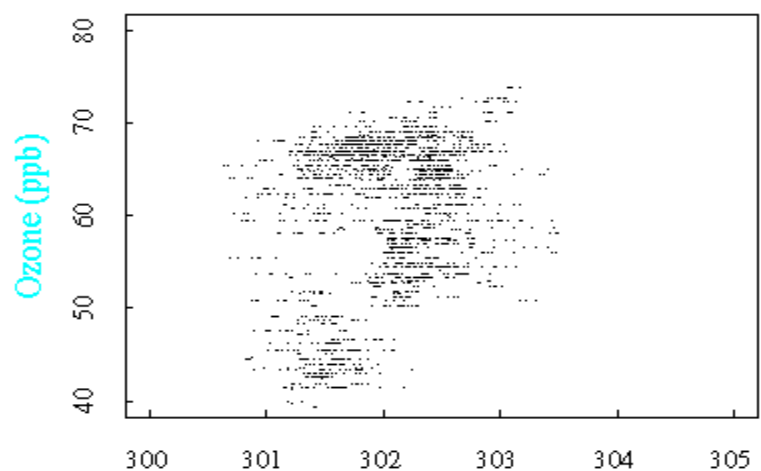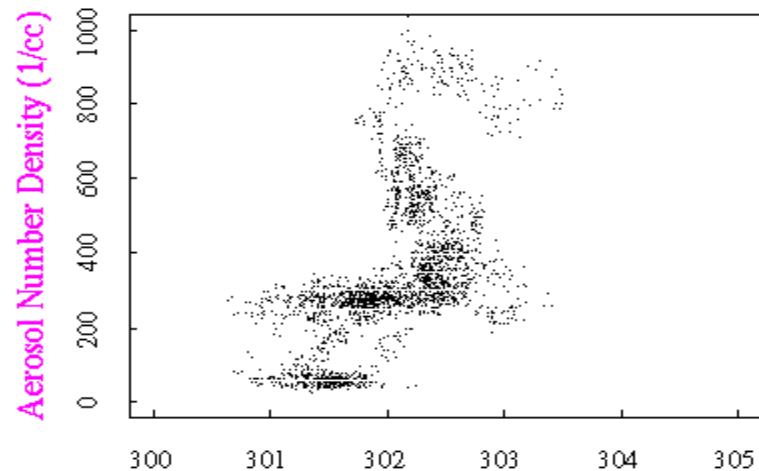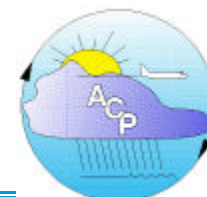
Heterogeneous Reaction Model

Assumptions:

1. Ozone reacts instantly upon accommodation on the aerosol surface.

2. Well-mixed ozone concentration at 75 ppb is assumed in the air mass at sunset, which was sampled 7 hours later in the night.

3. Air masses indicative of different origin (low ozone and low aerosol) are neglected.

Model Formulation:

$$d[O_3]/dt = -k A [O_3]$$

Where

k = mass transfer coefficient (cm/s)
A = aerosol surface area concentration (cm^2/cm^3)
$[O_3]$ = ozone concentration (ppb)
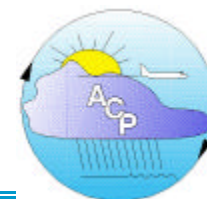
Mass Transfer Coefficient

Model 1: k independent of RH   Model 2: k dependent on RH

$1/k = R_p/D_{O3} + 4/(\alpha_1 v)$ $1/k = R_p/D_{O3} + 4/(\alpha_2 \, RH \, v)$

Using

R_p = 0.1 μm (avg aerosol radius)

D_{O3} = 0.17 cm^2/s (Diffusivity of O_3 in air)

v   = 3.5 X 10^4 cm/s (mean molecular speed of O_3 in air at 280 K)

α_1, α_2 = accommodation coefficients

Model Integration

$[O_3] = [O_3]_0 \exp(-k \, A\Delta t)$

For Flight B,

$[O_3]_0 = 75$ ppb (assumed initial concentration)

$\Delta t = 7$ hr (from sunset to sampling time)

Sep 1, 1998, Flight B, 3000 ft MSL
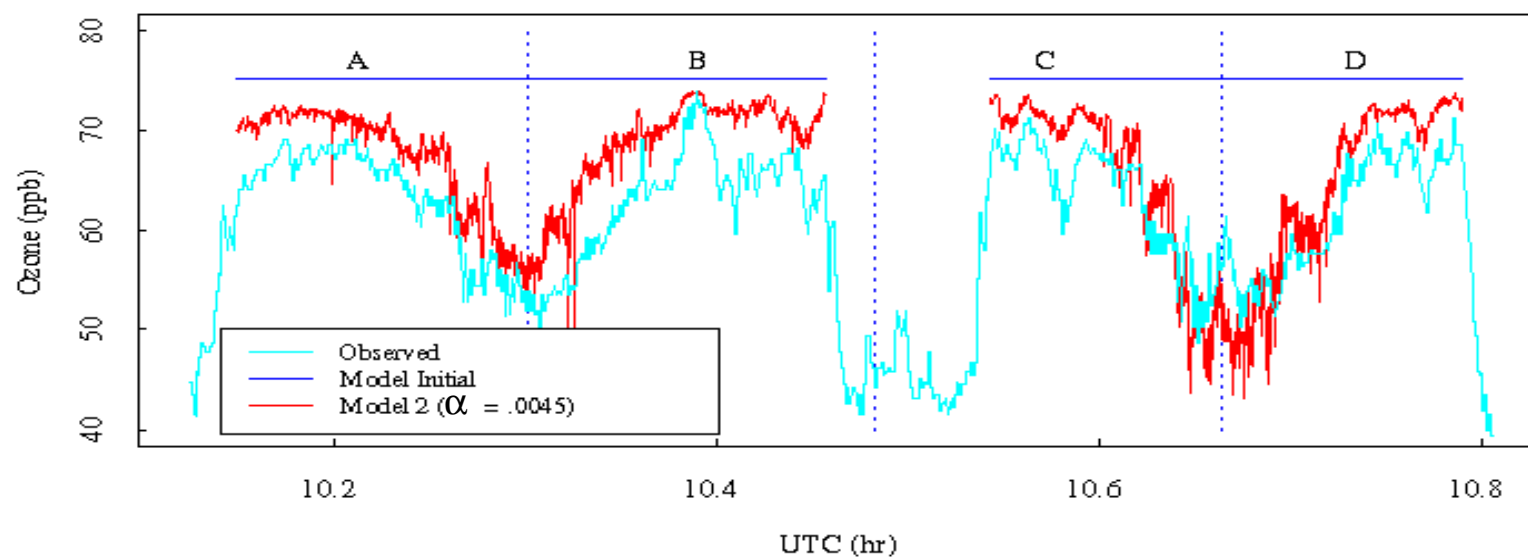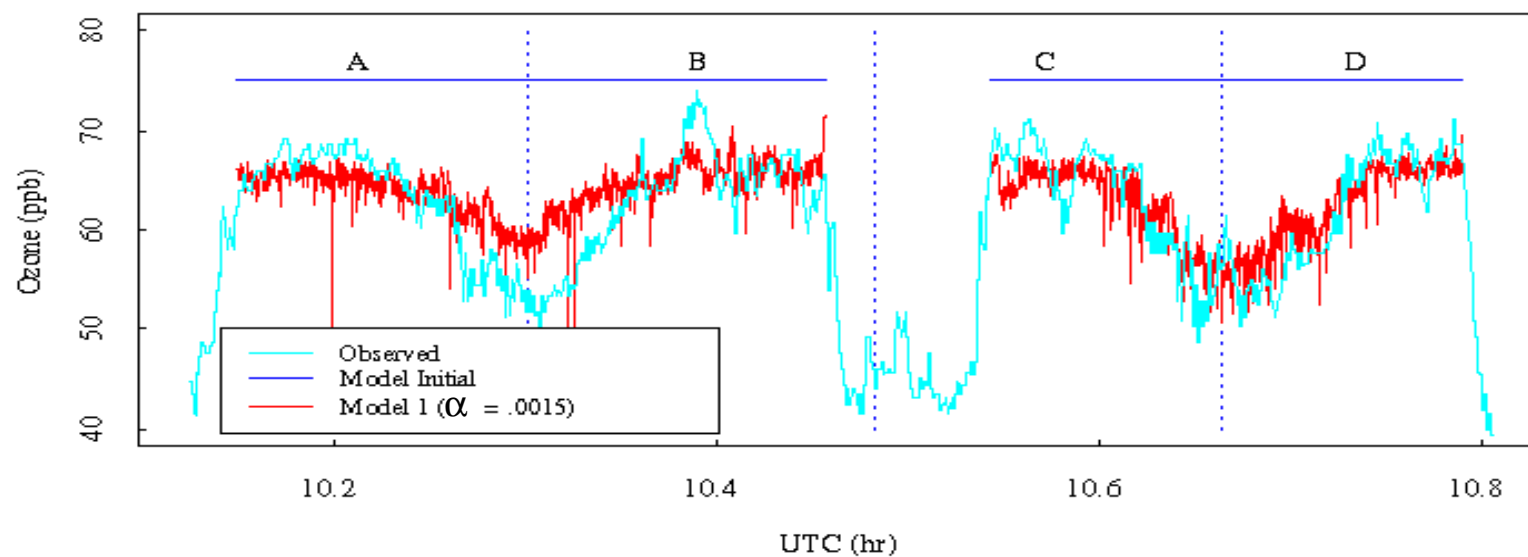
• Model 2 appears to capture the extent of ozone loss as well as some of the rapidly varying features in the ozone concentration profile; Model 1 does not simulate these features well.
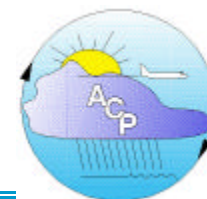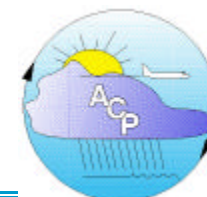• These results suggest that loss of ozone on aerosol surfaces may be strongly dependent not only on the amount of aerosol surface area available, but also on the ambient relative humidity which could change the wetness of the surface, and hence the accommodation coefficient of ozone on the surface.
• The values of the accommodation coefficient obtained here represent the upper limit due to the various assumptions involved. Nevertheless, these results suggest that appreciable ozone loss via heterogeneous reaction on aerosol surface could potentially occur, especially at night when photochemical production of ozone is absent.
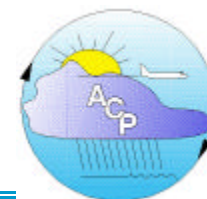
Hypothesis Testing: work in progress

Equilibrium model: Is observed behavior related to dissolution within aerosol "aqueous skin"?

H_2O H_2O H_2O H_2O H_2O H_2O

$\Delta\%RH=-10$
$\Delta x(O_3)=-10$ ppb

H_2O H_2O H_2O H_2O

$x_i(O_3)=60$ ppb $x_f(O_3)=50$ ppb
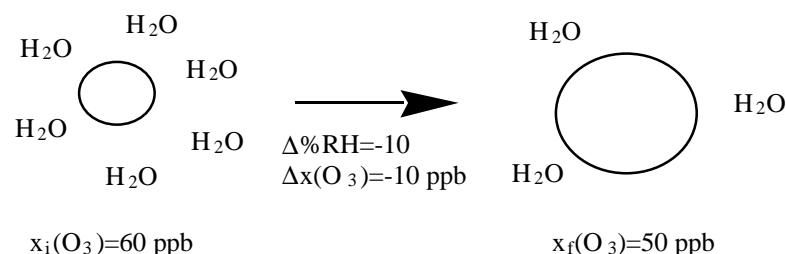
Assuming all O_3 into condensed water: 2.1×10^{-4} M (O_3)

Compare to H P $= 0.013$ M/atm 10^{-8} atm $= 1.3 \times 10^{-10}$ M (O_3)

♦ Since HP $<<$ M(O_3) based on dissolution model, Equilibrium dissolution cannot explain observed O_3 change with aerosol volume.

Size Distribution: What size aerosols dominate? Relationship to suspected heterogeneous activity?

Chemical Composition: Chemical nature of aerosols? N compounds present?

Statistical Analysis of time series: evaluate significance of correlations and anti-correlations
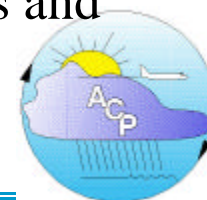
Laboratory Studies

A. Surface Science Studies

B. Aerosol Chamber Studies

C. Aerosol Analysis by Laser Desorption
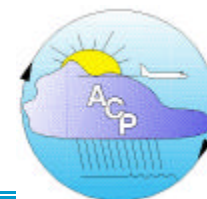
Lab Studies Objectives

- To find <u>number</u> of active sites on aerosol soots for various interconversioon or redox reactions of NO_2, HONO, N_2O_5, NO, $HN0_3$, O_3, H_2O

- To measure kinetics, α's of the reactions vs. T, P.

- To measure effects of humidity, simultaneous exposure to several species, aging.

- To integrate results with modeling, field studies
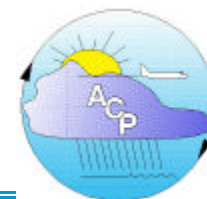
Surface Kinetic Studies of Collected Aerosols
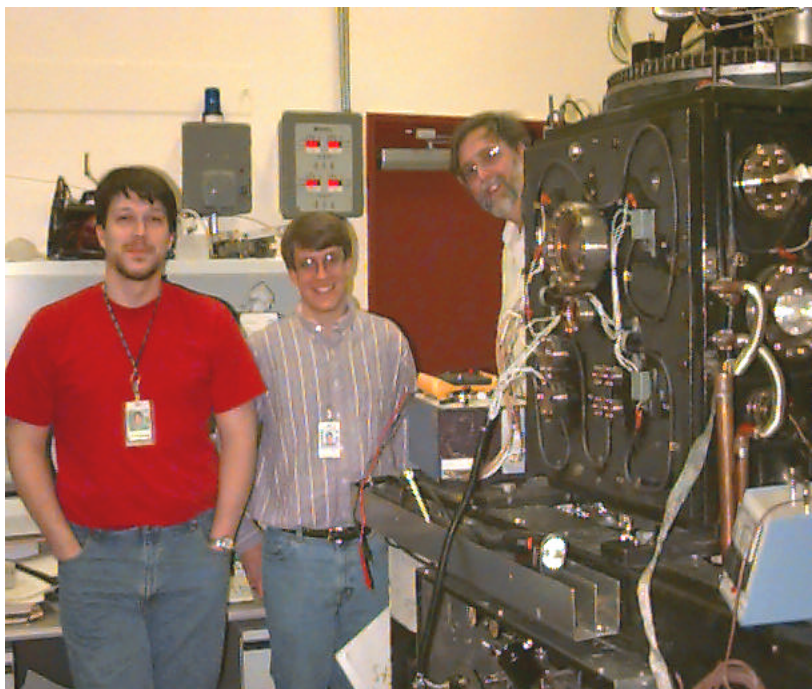
Study Renoxification, O_3 chemistry on collected soot's under wide range of T, with several gas species present.

Allows identifying non-linear kinetics, and better extrapolative behavior of measured kinetics.

Results compared to aerosol chamber results.

One technical problem: mass spectrometer interconversions

MASS SPECTROMETRY OF NO$_y$ MIXES
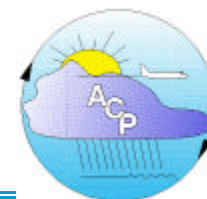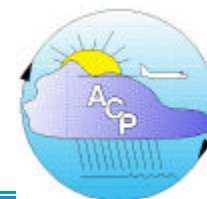
(MIKE CARPENTER, MARTIN IEDEMA, JIM COWIN)

- Mass spectrometry of mixes of NO$_2$, HNO$_2$, NO, N$_2$O$_5$, etc. are problematic due to their interconversion within the spectrometer.

- We have a novel solution: a pre-separation step based the relative sorptive binding to an inert "analyzer" surface.

- Heating the analyzer sequentially desorbs the various NO$_y$ species into the mass spectrometer. (Cracking still occurs within the mass spectrometer, but species identification is via the desorption temperature.)

- This will be used to analyze NO$_y$ conversion due to heterogeneous chemistry with soot particles .

Pacific Northwest National Laboratory

MS of NOy Mixes

analyzer

soot sample

HNO$_3$ GAS

RAMP TEMPERATURE OF ANALYZER

MASS SPECTROMETER

MASS SPECT. SIG., MASS 30

MIXED HNO$_3$ AND NO$_2$

NO$_2$ ALONE

HNO$_3$ ALONE

100   120   140   160   180   200

ANALYZER TEMPERATURE [K]
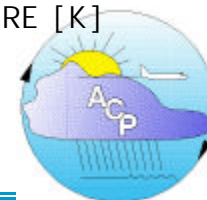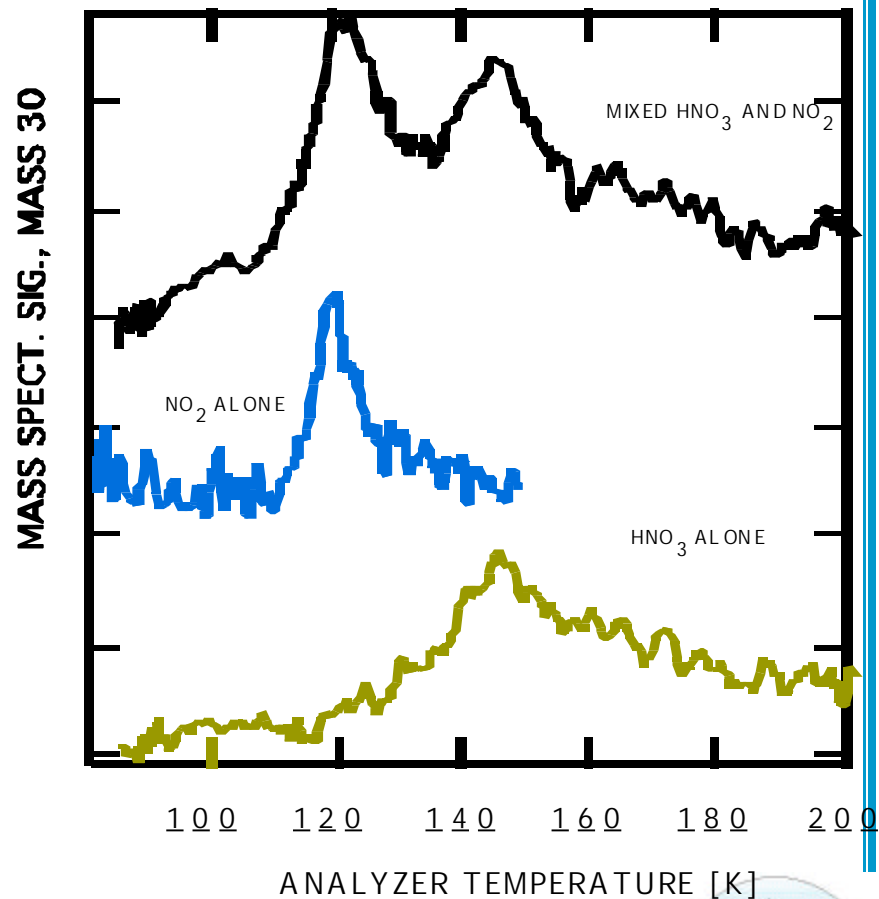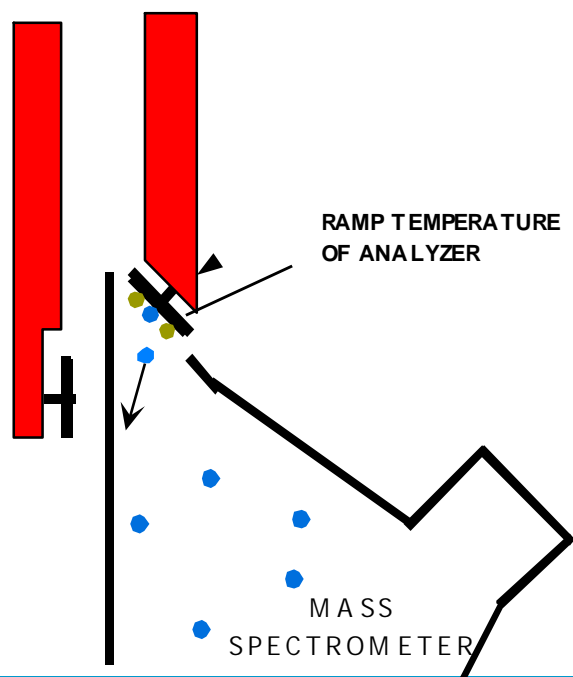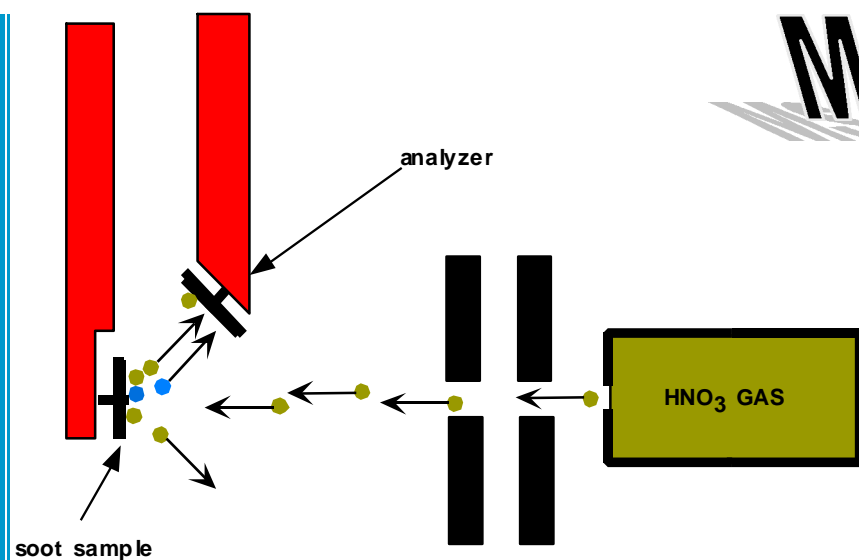
Chemistry: day and night
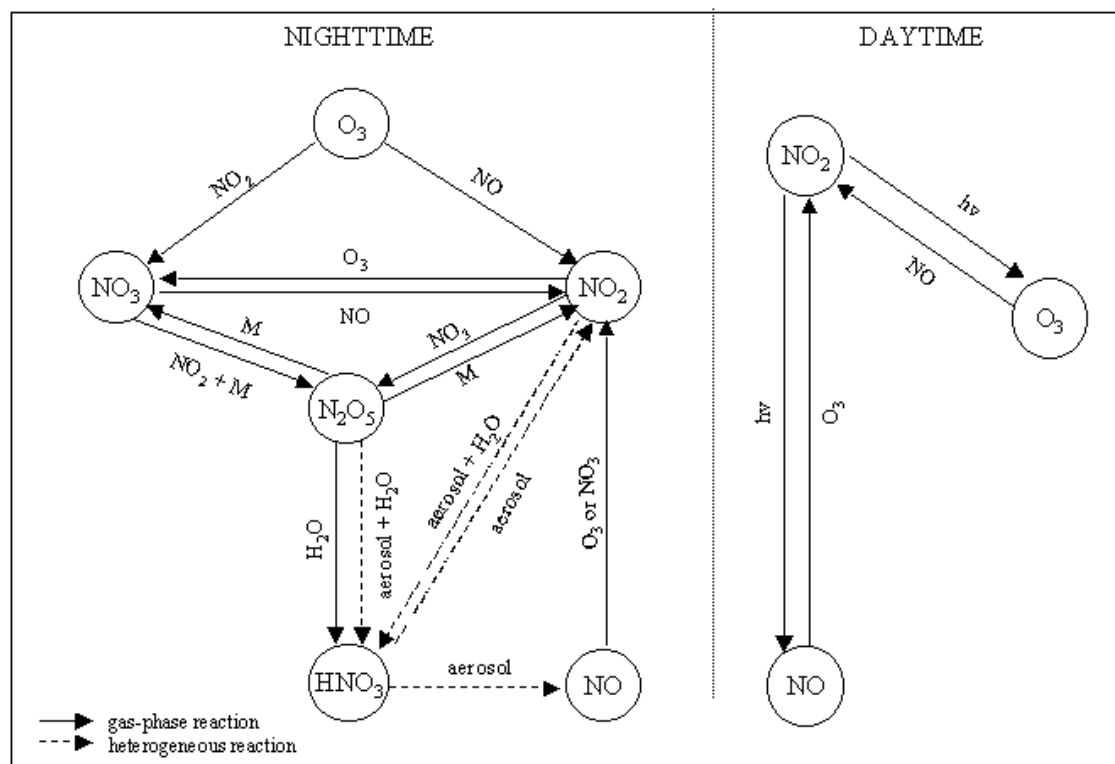
Monitor NOy mass budget at night, in conjunction with aerosol characteristics, to assess differences between key nighttime and daytime processes
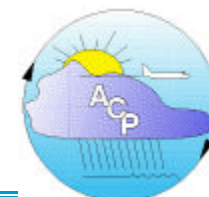
B. Aerosol Chamber Studies

Experimental Apparatus

Aerosol Inlet

Thermocouple feedthroughs

Dewar Vacuum

Inner Assembly

Vacuum Jacket

FTIR

White-cell Optics

Detector

Low temperature Liquid methanol inlet

0.5 m
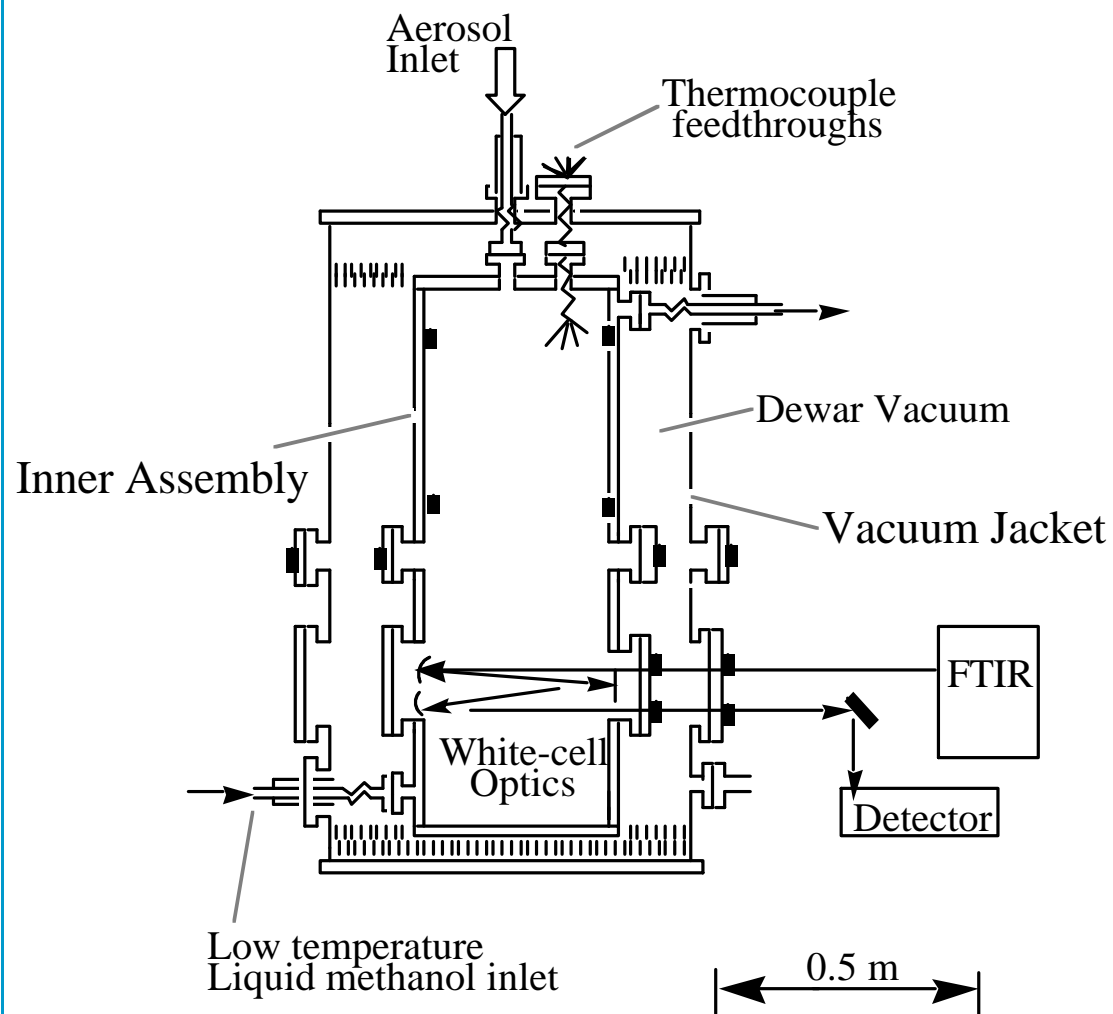
Investigators:
Mike Carpenter,
Rob Disselkamp

- Teflon-coated inner assembly is chemically inert
- Long pathlength infrared absorption spectroscopy used to probe aerosol sample

Aerosol Chamber Result: HNO_3 plus Soot

Does "Renoxification" Occur?

(i.e, does soot reduce HNO_3?)

- Soot consumes HNO_3 and produces NO_2!

Aerosol Chamber Result: HNO_3 plus Soot
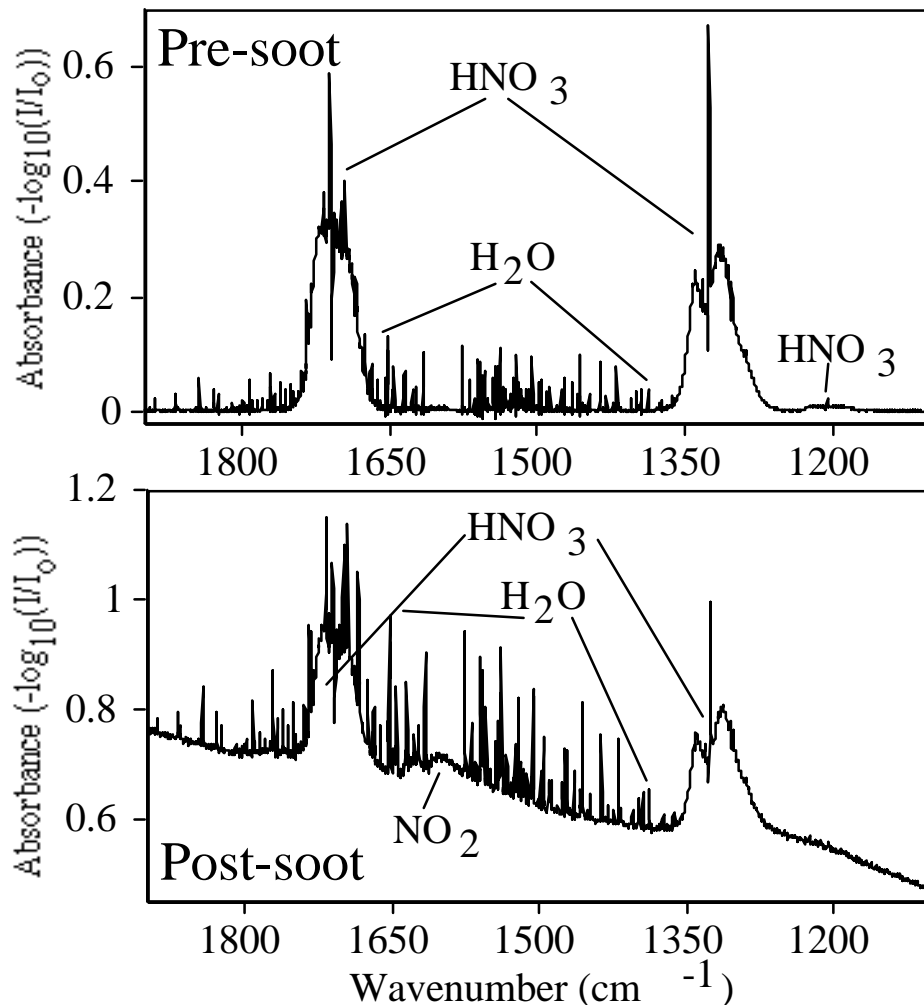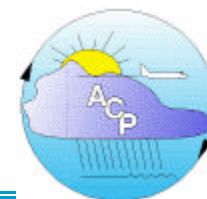
HNO_3 and NO_2 Partial Pressure versus time
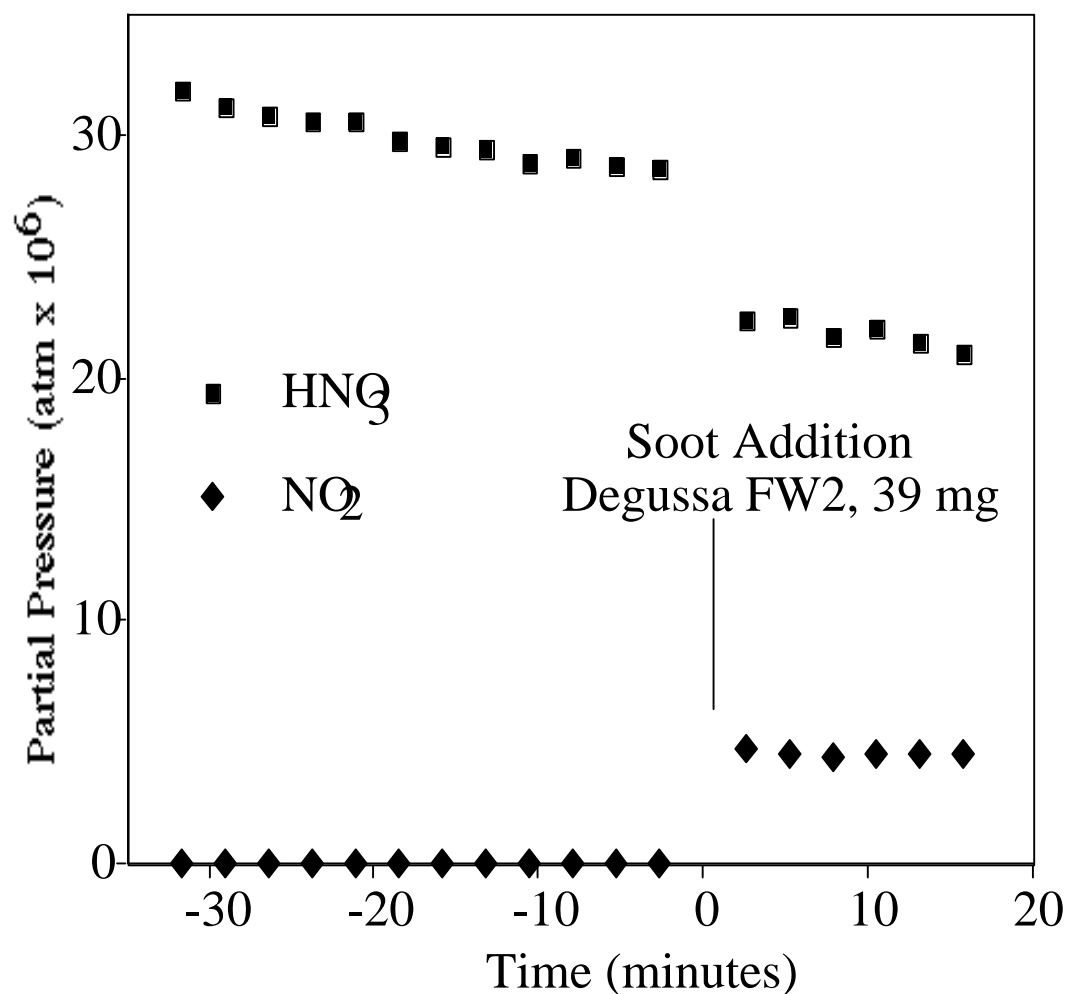
- HNO_3 uptake:NO_2 production = 1.3:1

- Active sites at soot surface are "titrated" by HNO_3 (i.e., continual uptake of HNO_3 *not* observed)
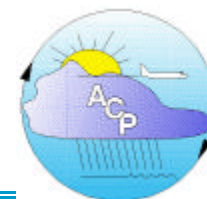
Aerosol Chamber Result: O_3 plus Soot

O_3 and CO_2 Partial Pressure versus Time
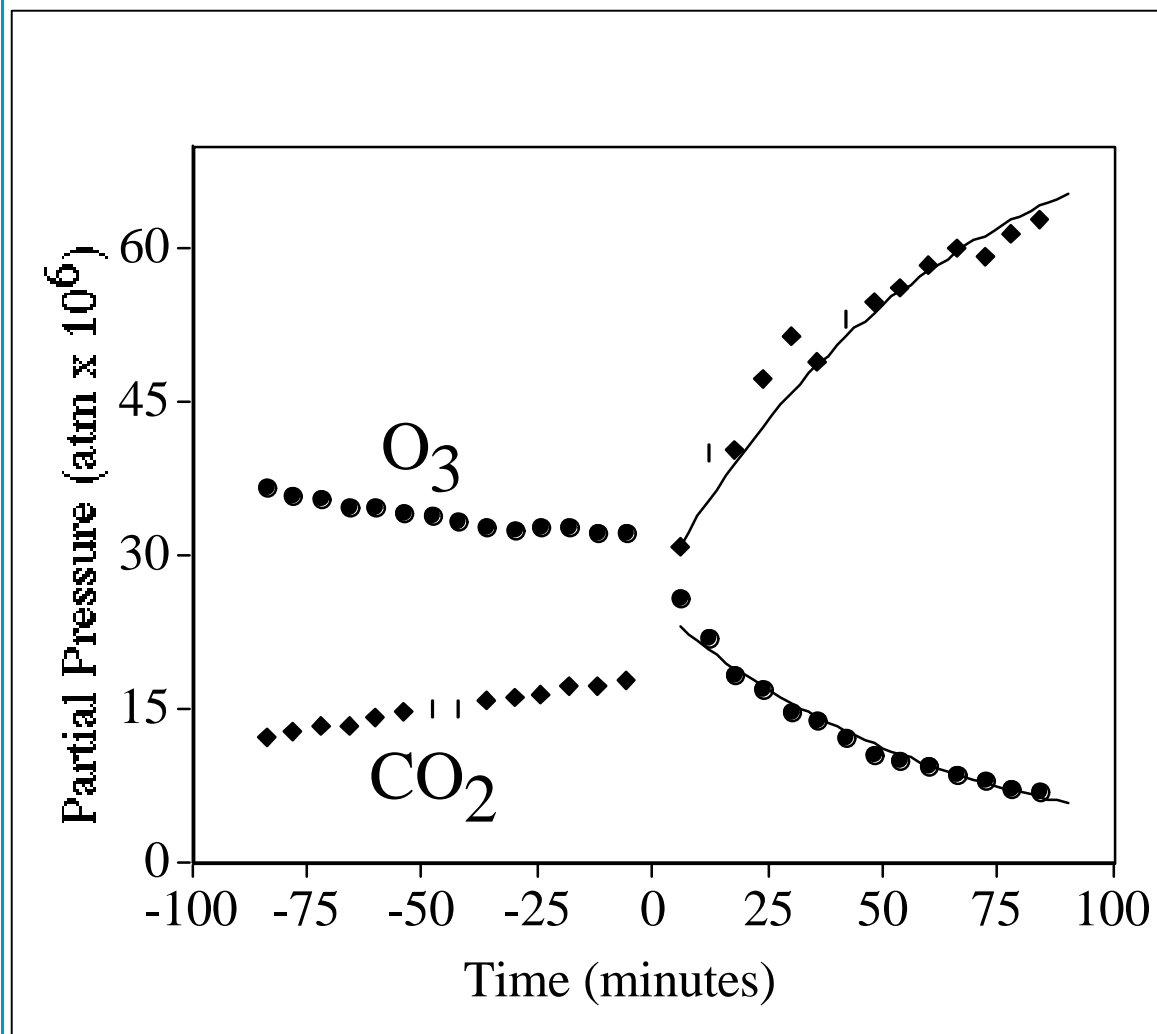
- CO_2 produced:O_3 consumed = 2:1 (*large* Q.Y.!)
- $\tau(O_3) \sim 100$ minutes at 10^{-6} gm/cm^3 soot, hence $\alpha = 10^{-8}$ so not an important atmospheric depletion process!

Future Direction: Questions

- How well do model derived accommodation coefficients agree with laboratory measurements? See accompanying panel on kinetic model studies.

- How much can the dissolution of ozone within an aerosol 'aqueous skin' explain the observed reduction of ozone in the presence of elevated aerosol surface area with high humidities? See accompanying panel

- What size aerosols dominate? What is the relationship to suspected heterogeneous activity?
  - Analyze PCASP, FSSP, CPC aerosol data in depth; relate to gaseous compounds

- What is the chemical nature of aerosols? Are nitrogen compounds present?
  - single particle analysis of selected filters; calculate aerosol quantities (e.g., extinction efficiency, conjugate albedo, Angstrom exponents) and compare with standard values.

- How significant are the observed correlations and anti-correlations?
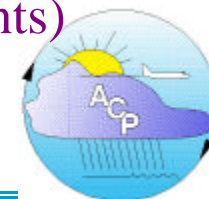
Future Direction: SOS/Nashville '99

- Southern Oxidants Study = long-term research program focusing on the formation of photochemical oxidants in the South

- Focus is on science questions with policy implications, including

  - how to characterize aerosols in urban and rural areas of the SOS region

  - how do nighttime meteorological and chemical processes influence rtes, efficiencies, and areal extent of ozone and fine particulate aerosol formation/accumulation?

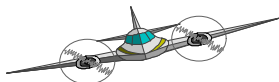- **Primary focus area = nighttime chemistry and dynamics**
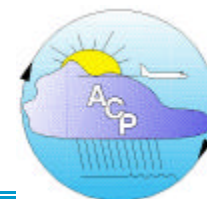
ACP Research Goals in Nashville

NOAA/CASA:
Remote sensing
of O3, aerosols

NOAA/P-3

DOE/G-1:

TVABell

profiler

Sfc.AQMS

- Nighttime Chemistry
  - NOy budget, ozone and aerosols
  - chemistry and dynamics of nocturnal planetary boundary layer
- Characterization of full diurnal cycle
  - Most field campaigns target daytime chemistry and dynamics
  - past SOS results: pollutant mix can be significantly affected by non-photochemical reactions that occur at night.
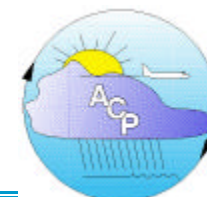 - Coordinated sampling with other participants (see accompanying panel.

Sampling the Full Diurnal Cycle
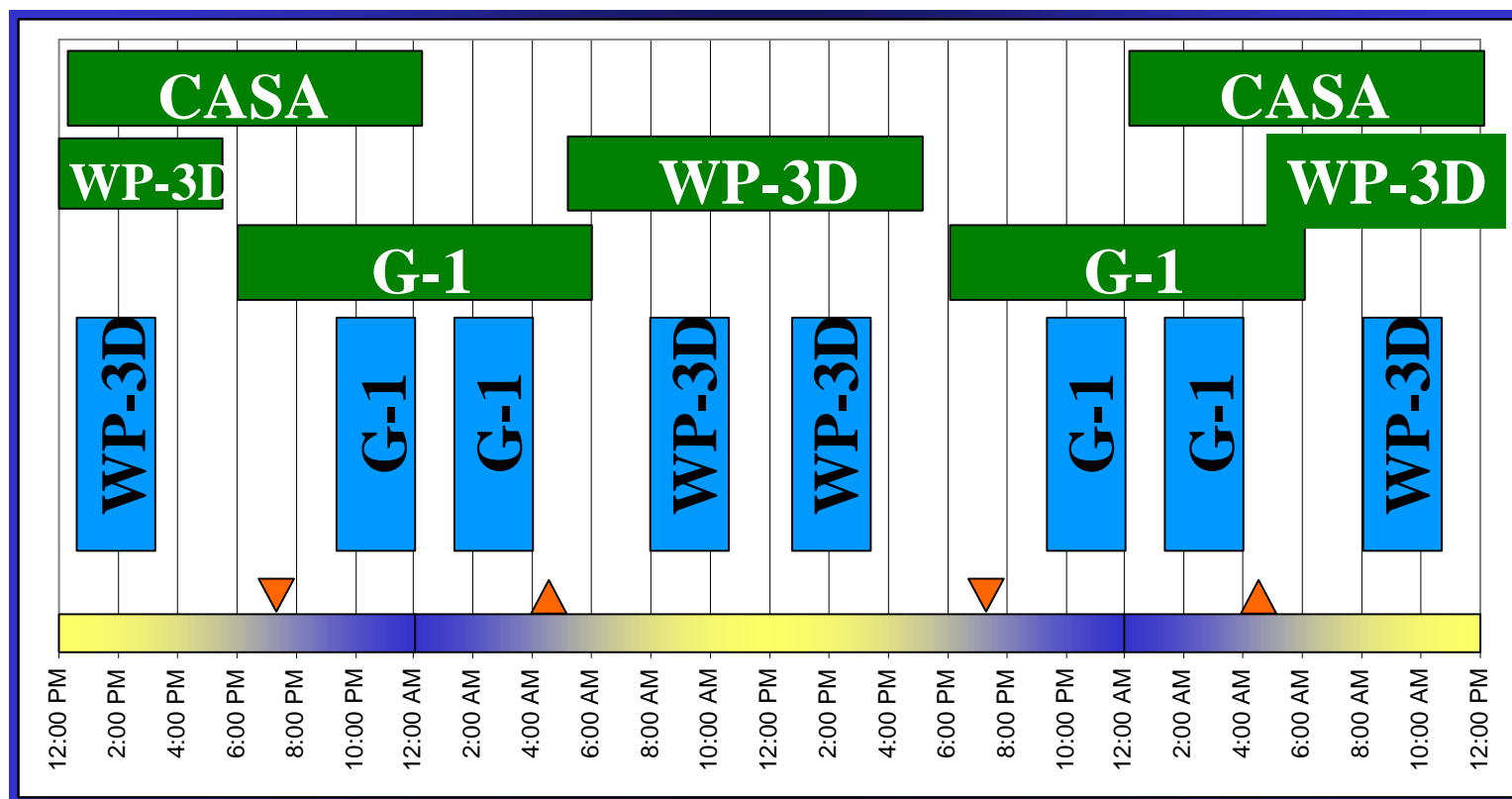
Preliminary Scientific Results and Their Significance

1) 15 to 20 ppb ozone depletion in presence of aerosols over 5 hr period	$\Rightarrow$ Significant loss term that's not in air quality models.
2) Successfully monitored nitrous and nitric acid using new, smaller mass spectrometer.	$\Rightarrow$ New measurement capability for this and other ACP campaigns; information important for assessing role of aerosols on oxidant levels.
3) Development of capability to look at 'renoxification' kinetics	$\Rightarrow$ Can address whether HNO3 is end product in chemical cycle, or if additional NOx can be produced from aerosols.
4) Examination of chemical reactivity of soot particles with ozone	$\Rightarrow$ Quantify rates for use in air quality models.